



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF : Takeshi IWASAKI

SERIAL NUMBER : 10/626,837

FOR : PERPENDICULAR MAGNETIC RECORDING MEDIUM  
AND MAGNETIC RECORDING/REPRODUCTION APPARATUS

FILED : July 25, 2003

GROUP ART UNIT : 1773

EXAMINER : Kevin M. BERNATZ, PhD

DECLARATION UNDER 37 C.F.R. 1.132

Hon. Commissioner for patents  
and trademarks

I, Takeshi Iwasaki, a Japanese citizen residing in Yokohama-shi, Kanagawa-ken, Japan, hereby declare and state that:

I completed the physics course of the Graduate School of Engineering Science, Osaka University, in March 2001, and joined TOSHIBA CORPORATION in April of the same year. Ever since I joined TOSHIBA CORPORATION, I have belonged to the Hard Disk Development Dept. of the Core Technology Center and engaged in the research and development of magnetic recording mediums.

## 1. Experiments

### Experiment 1

I prepared a nonmagnetic substrate made of a glass substrate for use as a 2.5-inch magnetic disk. The nonmagnetic substrate was placed in a vacuum chamber having a degree of vacuum of  $1 \times 10^{-5}$  Pa, and was heated until the temperature of the substrate became 250°C. In an Ar gas atmosphere having a gas pressure of 0.6 Pa, DC magnetron sputtering was executed. The nonmagnetic substrate was opposed to a target, and an electric discharge leading to the target was made to take place by application of DC 500W, so as to form a 40-nm Cr film. The Cr film was intended as a nonmagnetic undercoat layer used for a ferromagnetic layer. A CoCrPt ferromagnetic layer was formed on the Cr film in such a manner as to have a thickness of 25 nm. A CoZrNb soft magnetic backing layer having a thickness of 200 nm was formed on the resultant CoCrPt ferromagnetic layer.

The substrate was cooled until the substrate temperature lowers to room temperature. Subsequently, an electric discharge was made to take place by application of DC 300W, using Ti as a first undercoat layer. As a result, Ti layer having a thickness of 4 nm was formed on the CoZrNb soft magnetic backing layer. To form a second undercoat layer on the Ti layer, an electric discharge was made to take place by application of DC 500W, using Co-37at%Cr-8at%Pt. As a result, a nonmagnetic CoCrPt layer having a thickness of 20 nm was formed. Subsequently, a CoPtCrO perpendicular magnetic recording layer having a thickness of 15 nm was formed on the CoCrPt layer in an Ar gas atmosphere containing oxygen, using a target of Co-20at%Pt-16at%Cr. Then, a CoCrCe perpendicular magnetic recording layer having a thickness of 9 nm was formed, using a target of Co-20at%Cr-15at%Ce. Lastly, a C protective layer having a thickness of 7 nm was formed on the CoCrCe perpendicular magnetic recording layer. After films were successively formed in the vacuum chamber in this manner, the substrate was taken out into the atmosphere. In the atmosphere, a 1.5-nm layer of perfluoropolyether-based lubricant was formed by dipping, thereby obtaining a perpendicular magnetic recording medium.

A magnetic field of 15 kOe (about  $1.2 \times 10^6$  A/m) was applied outward in the

radial direction of the disk substrate of the perpendicular magnetic recording medium obtained as above, by using a magnetizing apparatus having an electromagnet, so that the CoCrPt ferromagnetic layer exhibiting longitudinal hard magnetism was magnetized in the radial direction. The magnetoresistance effect of the magnetized perpendicular magnetic recording medium was used to evaluate the recording/reproduction characteristics by using a single pole head having a recording track width of 0.3  $\mu\text{m}$  and a reproduction track width of 0.2  $\mu\text{m}$ . As a result, a differential waveform half width dPW50 (which was an index of the resolution) was 82 nm, and SNRm (S: low-frequency output, N: noise at 400 kFCI) was 23.0 dB, indicating that the medium was excellent. In addition, the decay value at a low-frequency output of 50 kFCI, which was a thermal decay index, was -0.07%/decade.

Similar advantages were observed with respect to perpendicular magnetic recording mediums that used, instead of cerium, yttrium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, thulium, ytterbium, and lutetium.

### **Comparative Experiment 1**

A CoPtO film was prepared by DC magnetron sputtering. A substrate was formed of glass for which chemical reinforcing processing was executed. A target was made of a Co-20at%Pt alloy having a diameter of 6.5 inches. The substrate and the target were placed in a DC magnetron sputtering apparatus, with the distance between them kept at 150 mm. Sputtering was executed to form a 50 nm-thick CoPt film in such a manner that the substrate temperature was kept at room temperature, the total sputtering pressure was 4 Pa, and the sputtering power was 1 kW for a diameter of 6.5 inches. Two kinds of sputtering gas, one was Ar gas without oxygen and the other was Ar gas containing 0.01% of oxygen, were alternately used such that the sputtering gas used was switched 20 number of times in one sputtering process.

Thereafter, the substrate was heated to 200°C, and Co-10at%Cr-15at%Pt-5at%Ce films (second magnetic films) each having a thickness of 50 nm were sequentially formed. A 10 nm-thick carbon protective film was formed on the resultant

multi-layered film medium.

### **Comparative Experiment 2**

After being washed, a glass substrate was placed in a sputtering apparatus, and the sputtering apparatus was evacuated until the degree of vacuum became  $2 \times 10^{-7}$  Torr. Subsequently, the substrate was heated to 200°C, so as to form a undercoat layer of Ti-10at%Cr having a thickness of 30 nm. The undercoat layer is used for controlling the structure of magnetic films. The undercoat layer had a hcp structure, and its crystalline orientation was  $\langle 00 \cdot 2 \rangle$ .

A CoPtO film having a thickness of 50 nm was formed on the TiCr film. A target was made of a Co-20at%Pt alloy. The substrate and the target were placed in a DC magnetron sputtering apparatus, with the distance between them kept at 150 mm. After the substrate was cooled to room temperature, sputtering was executed to form a 50 nm-thick CoPtO film in such a manner that the total sputtering pressure was 4 Pa, and the sputtering power was 1 kW. Two kinds of sputtering gas, one was Ar gas without oxygen and the other was Ar gas containing 0.01% of oxygen, were alternately used such that the sputtering gas used was switched 20 number of times in one sputtering process.

Thereafter, the substrate was heated to 200°C, and Co-10at%Cr-15at%Pt-5at%Ce magnetic films each having a thickness of 50 nm were sequentially formed. A 10 nm-thick carbon protective film was formed on the resultant multi-layered film medium.

### **Comparative Experiment 3**

A undercoat substrate formed of glass was prepared and placed in an atmosphere wherein the Ar pressure was  $8 \times 10^{-2}$  Torr. The undercoat substrate was kept at room temperature. In this state, a magnetic layer, which was made of an alloy containing 18.5 wt% of Cr, 0.5 wt% of Pr (rare earth element) and the balance being Co, was deposited by high-frequency sputtering over the upper surface of the undercoat substrate in such a manner that the magnetic layer had a thickness between 1  $\mu$ m and

2  $\mu\text{m}$ . In this way, a perpendicular magnetic recording medium was prepared. The deposition rate was 1  $\mu\text{m/hr}$ .

#### **Comparative Experiment 4**

A CoPtO film was formed by DC magnetron sputtering as follows. A substrate was formed of glass for which chemical reinforcing processing was executed. A target was made of a Co-20at%Pt alloy having a diameter of 6.5 inches. The substrate and the target were placed in a DC magnetron sputtering apparatus, with the distance between them kept at 150 mm. Sputtering was executed to form a 50 nm-thick CoPt film in such a manner that the substrate temperature was kept at room temperature, the total sputtering pressure was 4 Pa, and the sputtering power was 1 kW for a diameter of 6.5 inches. By this sputtering, a CoPt film having a thickness of 50 nm was formed. Two kinds of sputtering gas, one was Ar gas without oxygen and the other was Ar gas containing 0.01% of oxygen, were alternately used such that the sputtering gas used was switched 20 number of times in one sputtering process.

Thereafter, the undercoat substrate was kept at a temperature between 100°C and 200°C in an atmosphere wherein the Ar pressure was  $8 \times 10^{-2}$  Torr. In this state, a magnetic layer, which was made of an alloy containing 18.5 wt% of Cr, 0.5 wt% of Pr (rare earth element) and the balance being Co, was deposited by high-frequency sputtering over the upper surface of the undercoat substrate in such a manner that the magnetic layer had a thickness between 1  $\mu\text{m}$  and 2  $\mu\text{m}$ . In this way, a perpendicular magnetic recording medium was prepared. The deposition rate was 1  $\mu\text{m/hr}$ .

#### **Comparative Experiment 5**

After being washed, a glass substrate (commercially available from Ohara Inc., Japan, outer diameter: 2.5 inches) was placed in a film forming chamber of a DC magnetron sputtering apparatus (Model: C-3010 commercially available from ANELVA, Japan), and the chamber was evacuated until the degree of vacuum became  $1 \times 10^{-5}$  Pa. A soft magnetic backing layer having a thickness of 100 nm was formed on the glass substrate by sputtering. A target made of 89Co4Zr7Nb (which contained 89 at%

of Co, 4 at% of Zr and 7 at% of Nb) was used for this sputtering, and the substrate was kept at a temperature not higher than 100°C. By use of a vibration type magnetic characteristic measuring apparatus (VSM), it was confirmed that the mathematical product  $B_s \cdot t$  (T · nm) of the saturated flux density  $B_s(T)$  of the soft magnetic backing layer and the thickness  $t(\text{nm})$  thereof was 120 (T · nm).

After the substrate was heated to 200°C, an orientation control layer having a thickness of 20 nm was formed on the soft magnetic backing layer by using a Ru target, and an intermediate film having a thickness of 5 nm was formed by using a 65Co30Cr5B (which contained 65 at% of Co, 30 at% of Cr and 5 at% of B) target. Thereafter, the substrate was cooled to room temperature.

Perpendicular magnetic layers, each having a thickness of 20 nm, were sequentially formed, using 68Co18Cr10Pt4Nd (which contained 68 at% of Co, 18 at% of Cr, 10 at% of Pt, and 4 at% of Nd) target. In the above sputtering process, Ar was used as a film-formation sputtering gas, and the pressure was kept at 0.6 Pa. Then, a protective layer having a thickness of 5 nm was formed by CVD (Chemical Vapor Deposition). Then, a lubricating layer formed of perfluoropolyether was formed by dipping, thereby obtaining a magnetic recording medium.

### **Comparative Experiment 6**

Experiments regarding Hikosaka (US 5,792,564) and Sakawaki (2003/0082407) (See Example 8 of Hikosaka and Example 17 of Sakawaki)

After being washed, a glass substrate (commercially available from Ohara Inc., Japan, outer diameter: 2.5 inches) was placed in a film forming chamber of a DC magnetron sputtering apparatus (Model: C-3010 commercially available from ANELVA, Japan), and the chamber was evacuated until the degree of vacuum became  $1 \times 10^{-5}$  Pa. A soft magnetic backing layer having a thickness of 100 nm was formed on the glass substrate by sputtering. A target made of 89Co4Zr7Nb was used for this sputtering, and the substrate was kept at a temperature not higher than 100°C. By use of a vibration type magnetic characteristic measuring apparatus (VSM), it was confirmed that the mathematical product  $B_s \cdot t$  (T · nm) of the saturated flux density

Bs(T) of the soft magnetic backing layer and the thickness  $t(\text{nm})$  thereof was 120 (T · nm). Next, the resultant structure was exposed to oxygen gas. More specifically, the resultant structure was exposed to an Ar gas atmosphere containing 50% of oxygen, and left to stand in that atmosphere at 1 Pa for 10 seconds.

After the substrate was heated to 200°C, an orientation control layer having a thickness of 20 nm was formed on the soft magnetic backing layer by using a Ru target, and an intermediate film having a thickness of 5 nm was formed by using a 65Co30Cr5B target.

A CoPtO film was formed as a first perpendicular magnetic layer. A Co-20at% Pt alloy was used as a target. The substrate and the target were placed in a DC magnetron sputtering apparatus, with the distance between them kept at 150 mm. Sputtering was executed to form a 50 nm-thick CoPtO film in such a manner that the substrate temperature was kept at room temperature, the total sputtering pressure was 4 Pa, and the sputtering power was 1 kW. By this sputtering, a CoPtO film having a thickness of 50 nm was formed. Two kinds of sputtering gas, one was Ar gas without oxygen and the other was Ar gas containing 0.01% of oxygen, were alternately used such that the sputtering gas used was switched 20 number of times in one sputtering process.

The substrate was heated to 200°C, and second perpendicular magnetic layer, each having a thickness of 5 nm, were sequentially formed using a 59at%Co-22at%Cr-14at%Pt-5at%Nd target. In the above sputtering process, Ar was used as a film-formation sputtering gas, and the pressure was kept at 0.6 Pa. Then, a protective layer having a thickness of 5 nm was formed by CVD. Then, a lubricating layer formed of perfluoropolyether was formed by dipping, thereby obtaining a magnetic recording medium.

## 2. Conclusion

(1) The compositions of the magnetic recording mediums of the Experiment and the Comparative Experiments will be described. The composition of the magnetic recording medium was glass substrate/CoPtO formed at room temperature/CoCrPtCe/C

in Comparative Experiment 1, and was glass substrate/TiCr/CoPtO formed at room temperature/CoCrPtCe/C in Comparative Experiment 2. In contrast, the composition of the magnetic recording medium was glass substrate/Cr/CoCrPt/CoZrNb/Ti/CoCrPt/CoCrPtO formed at room temperature/CoCrCe formed at room temperature/C in Experiment 1.

A differential waveform half width dPW50 (which was an index of the resolution) was 82 nm in Experiment 1 related to the present invention, was 124 nm in Comparative Experiment 1, and was 118 nm in Comparative Experiment 2. The resolution was more improved in Experiment 1 than in Comparative Experiment 1 and Comparative Experiment 2.

SNRm (S: low-frequency output, N: noise at 400 kFCI) was 23.0 dB in Experiment 1 related to the present invention, was 8dB in Comparative Experiment 1, and was 12 dB in Comparative Experiment 2. This indicated that the thermal decay resistance was more improved in Experiment 1 than in Comparative Experiment 1 and Comparative Experiment 2.

The decay value at a low-frequency output of 50 kFCI, which was a thermal decay index, was -0.07%/decade in Experiment 1 related to the present invention, was -0.25%/decade in Comparative Experiment 1, and was -0.20%/decade in Comparative Experiment 2. This indicated that the thermal decay resistance was more improved in Experiment 1 than in Comparative Experiment 1 and Comparative Experiment 2.

(2) The composition of the magnetic recording medium was glass substrate/CoCrPr formed at room temperature/C in Comparative Experiment 3, and was glass substrate/CoPtO formed at room temperature/CoCrPr/C in Comparative Experiment 4. In contrast, the composition of the magnetic recording medium was glass substrate/Cr/CoCrPt/CoZrNb/Ti/CoCrPt/CoCrPtO formed at room temperature/CoCrCe formed at room temperature/C in Experiment 1.

A differential waveform half width dPW50 (which was an index of the resolution) was 82 nm in Experiment 1 related to the present invention, was 129 nm in Comparative Experiment 3, and was 120 nm in Comparative Experiment 4. This indicated that the resolution was more improved in Experiment 1 than in Comparative



Experiment 3 and Comparative Experiment 4.

SNR<sub>m</sub> (S: low-frequency output, N: noise at 400 kFCI) was 23.0 dB in Experiment 1 related to the present invention, was 6 dB in Comparative Experiment 3, and was 11 dB in Comparative Experiment 4. This indicated that the thermal decay resistance was more improved in Experiment 1 than in Comparative Experiment 3 and Comparative Experiment 4.

The decay value at a low-frequency output of 50 kFCI, which was a thermal decay index, was -0.07%/decade in Experiment 1 related to the present invention, was -0.24%/decade in Comparative Experiment 3, and was -0.22%/decade in Comparative Experiment 4. This indicated that the thermal decay resistance was more improved in Experiment 1 than in Comparative Experiment 3 and Comparative Experiment 4.

(3) The composition of the magnetic recording medium was glass substrate/CoZrNb/Ru/CoCrB/CoCrPtNd/C formed at room temperature/C in Comparative Experiment 5, and was glass substrate/CoZrNb/Ru/CoCrB/CoPtO formed at room temperature/CoCrPtNd/C in Comparative Experiment 6. In contrast, the composition of the magnetic recording medium was glass substrate/Cr/CoCrPt/CoZrNb/Ti/CoCrPt/ CoCrPtO formed at room temperature/CoCrCe formed at room temperature/C in Experiment 1.

A differential waveform half width dPW<sub>50</sub> (which was an index of the resolution) was 82 nm in Experiment 1 related to the present invention, was 118 nm in Comparative Experiment 5, and was 109 nm in Comparative Experiment 6. This indicated that the resolution was more improved in Experiment 1 than in Comparative Experiment 5 and Comparative Experiment 6.

SNR<sub>m</sub> (S: low-frequency output, N: noise at 400 kFCI) was 23.0 dB in Experiment 1 related to the present invention, was 6 dB in Comparative Experiment 5, was 14 dB in Comparative Experiment 1 and was 17 dB in Comparative Experiment 6. This indicated that the thermal decay resistance was more improved in Experiment 1 than in Comparative Experiment 5 and Comparative Experiment 6.

The decay value at a low-frequency output of 50 kFCI, which was a thermal decay index, was -0.07%/decade in Experiment 1 related to the present invention, was

-0.18%/decade in Comparative Experiment 5, and was -0.13%/decade in Comparative Experiment 6. This indicated that the thermal decay resistance was more improved in Experiment 1 than in Comparative Experiment 5 and Comparative Experiment 6.

(4) In the perpendicular magnetic recording medium of the present invention, the first perpendicular magnetic recording layer is formed at room temperature and contains cobalt and oxygen. The first perpendicular magnetic recording layer is of a segregated structure having magnetic crystal grains and grain boundaries. A second perpendicular magnetic recording layer is formed on the first perpendicular magnetic recording layer at room temperature. The second perpendicular magnetic recording layer mainly contains a crystalline alloy containing a rare earth element and a transition metal. With this structure, magnetic crystal grains grown from the first perpendicular magnetic recording layer are allowed to grow without any restrictions. Accordingly, the perpendicular magnetic recording medium is improved in crystal orientation.

In contrast, a perpendicular magnetic recording medium comprising a single perpendicular magnetic recording layer (i.e., a medium that does not comprise a perpendicular magnetic recording layer formed at room temperature and containing cobalt and oxygen) does not have an improved crystal orientation because a rare earth metal is diffused in magnetic crystal particles. Even if film formation is performed at room temperature, this does not improve the crystal orientation.

Even if the second perpendicular magnetic recording layer is formed at high temperature on the first perpendicular magnetic recording layer that is formed at room temperature and containing cobalt and oxygen, the crystalline orientation is not improved.

I, the undersigned, declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

Date *January 18, 2006*

*Takeshi Iwasaki*

---

Takeshi Iwasaki